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The Photo-Polymerization of Styrene and Vinyl Acetate

A DISSERTATION

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ARTHUR A. VERNON

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THE PHOTO-POLYMERIZATION OF STYRENE AND VINYL ACETATE

In a number of oxidation processes sensitive to light the chain reaction theory has been shown to account satisfactorily for the phenomenon of inhibition of oxidation in such systems. An examination of the quantum yield of these photo-reactions shows that a large number of molecules react per light quantum absorbed, that the light absorbed, therefore, starts a chain of secondary oxidation processes. It has been known now for some time that many polymerization processes are light sensitive and also show the phenomenon of inhibition by added agents. Thus far, however, quantitative studies similar to those with oxidation reactions have been lacking. An additional interest attaches to such studies with processes of polymerization. It has been shown by Alyea and Bäckström,[1] in certain reactions, that the inhibitor in oxidation processes is oxidized in the process of breaking the reaction chains. Such a fate for the inhibitor molecule is impossible in polymerization processes carried out in the absence of oxygen. The question suggests itself, therefore, as to the nature of the inhibitory act in a polymerization reaction. It was to gain some insight into the quantitative aspects of the photo-polymerization that the following studies were made.

Only recently has any attention been given to the quantitative side of the question although references to qualitative experiments and reaction products are frequent. The theoretical side of the polymerization has drawn attention more recently as is indicated by the work of Carothers,[2] Staudinger[3] and Moureu and Dufraisse.[4]

[1] Alyea and Bäckström, *J. Am. Chem. Soc.*, **51**, 90–109 (1929).

[2] Carothers, *ibid.*, **51**, 2548 (1929).

[3] Staudinger, *Ber.*, **62**, 2893 (1929); **62**, 2933 (1929).

[4] Moureu and Dufraisse, *Bull. soc. chim. France*, [4] **35**, 1564 (1924). Since the completion of this work an article has appeared by Starkweather and G. B. Taylor [*J. Am. Chem. Soc.*, **52**, 4708 (1930)] describing experiments made to determine the kinetics of the thermal polymerization of vinyl acetate.

In order to broaden the scope of the investigation, two compounds—styrene and vinyl acetate—were used to study the photochemical polymerization process. Both of these compounds contain an ethylenic bond but oxygen is present in only one.

Experimental Details

Apparatus.—In most of the experimental work, the source of illumination was a vertical mercury arc of the Cooper–Hewitt type operating at about 175 watts. The liquids were illuminated in Pyrex reaction vessels made from tubing 2 cm. in diameter and 15 cm. long. By means of a ground-glass joint at the top, an inlet tube was immersed in the liquid to within 1 cm. of the bottom. An outlet was provided by a tube in the Pyrex vessel 2 cm. below the ground-glass joint. Both inlet and outlet tubes were provided with stopcocks. The liquid under study could be thoroughly flushed out by allowing a stream of oxygen-free hydrogen to pass in the inlet tube and out at the outlet tube. By closing the stopcocks the liquid could be sealed in an atmosphere of hydrogen and the reaction carried out under these conditions. This procedure was necessary since oxygen was found to influence the reactions and their velocities.

To obtain several checks on each experiment as rapidly as possible, a round copper vessel 10 cm. in diameter and 15 cm. high was used. Through the center of this was fastened by means of a water-tight joint a quartz tube about 2.5 cm. in diameter. The vertical mercury arc was supported in this tube. Water was circulated in and out of the copper vessel and, by means of a heater, any desired temperature up to 100° could be maintained.

Measurement of Reaction Rate.—A method was used which was suggested by Dr. G. B. Kistiakowsky. One cubic centimeter of the original solution was dissolved in a given amount of benzene and the freezing point of the benzene determined by the usual Beckmann method. After illumination, the same procedure was followed. In this case, the depression was less due to polymerization. Since the molecular weight of the polymer is at least of the order of 3000–4000,[5,6] it can safely be assumed that the effect of the polymeric molecules upon the freezing point of the benzene is negligible as compared with that of the rest of the molecules present. From the differences in the depression of the freezing point of benzene before and after illumination, the amount polymerized could be calculated. These measurements were supplemented by viscosity determinations on the same solutions.

Materials Employed.—In the experiments with styrene, a commercial preparation consisting of a 46% solution of styrene in ethylbenzene, supplied by the U. S. Rubber Company, was employed. To prepare the solution for illumination, the mixture was steam distilled in a partial atmosphere of hydrogen after the system had been freed of oxygen. The distillate was separated from the water, dried over oxygen-free calcium chloride and stored over hydrogen in a ground-glass stoppered bottle. The final styrene content of the purified solutions was determined by polymerizing the styrene with stannic chloride, precipitating the polymer in ethyl alcohol, filtering, drying and weighing.

For the experiments with vinyl acetate, a 30% solution by volume of vinyl acetate in ethyl acetate was employed. The vinyl acetate was kindly supplied by the Union Carbide and Carbon Chemical Corporation and the ethyl acetate was of high grade. In preparing these solutions for illumination, each constituent was distilled in hydrogen separately, the two were mixed in an atmosphere of hydrogen and stored over hydrogen.

[5] Stobbe and Posnjak, *Ann.*, **371**, 259 (1909).

[6] Staudinger, *Ber.*, **59**, 3019 (1926).

Experimental Results

Influence of Oxygen on Polymerization.—This was determined by separating a solution of styrene into two parts. One part was stored over hydrogen and the other part over oxygen. Samples were removed at various intervals and allowed to undergo photo-polymerization at 100° under identical conditions. No correction for thermal polymerization was made in these tests, the results of which are given in Table I.

TABLE I

EFFECT OF OXYGEN ABSORPTION ON PHOTO-POLYMERIZATION OF STYRENE

Time of storage, hours	Contact with H_2, % polymerized per hr.	Contact with O_2, % polymerized per hr.
0	6.39	6.39
48	6.50	9.14
96	6.20	9.15
144	5.85	10.25

This summary shows the acceleration due to absorbed oxygen and also the degree of constancy of result obtained when the mixture stands in contact with hydrogen. In all succeeding experiments, values within 10% of those indicated above for contact with hydrogen were recorded.

A further check upon this point was made by testing a solution which had been distilled in vacuum after having been steam-distilled in oxygen-free hydrogen. The results of this experiment indicated a polymerization rate which was within 10% of those given in Table I for contact with hydrogen.

The conclusion from these results is evident. Light alone may cause polymerization of styrene and the true rate of the photo-process is obtained with the hydrogen-distilled samples. That oxidation of styrene, whether thermal or photochemical, is also accompanied by polymerization is evident and, hence, the results of the polymerization of solutions stored over oxygen indicate a sum total of both of these effects. Table I shows that the increase due to complete oxygen saturation is about 50%; but the polymerization due to a very small percentage of oxygen in the hydrogen-prepared solution would be negligible as compared with that due to the ultraviolet light.

TABLE II

EFFECT OF OXYGEN ABSORPTION ON PHOTO-POLYMERIZATION OF VINYL ACETATE

Time of storage, hours	Contact with H_2, % polymerized per hour	Contact with O_2, % polymerized per hour
0	29.0	29.0
18		20.0
24	29.0	
48		12.0
90	29.5	
114		2.0
138	32.0	

The effect of oxygen upon the polymerization of vinyl acetate is different. Here oxygen inhibits the polymerization. The tests upon vinyl acetate solutions were made in the same way as were those with styrene. The results of these tests are embodied in Table II.

Effect of Temperature on Polymerization Velocity.—Using the method as outlined previously, photo-polymerizations were made at temperatures of 30, 70 and 100° in the case of styrene and at 40 and 70° in the case of vinyl acetate solutions. The curves for Fig. 1 and Fig. 2 are plotted from

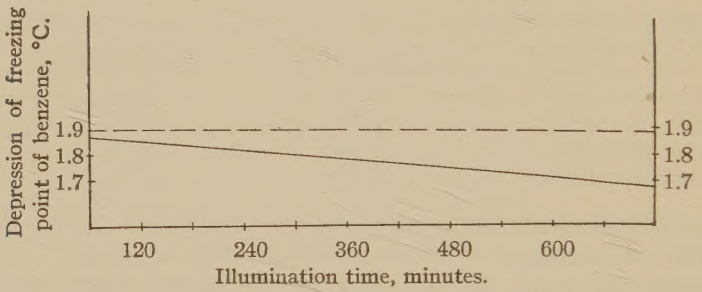

Fig. 1.—Polymerization of styrene–ethylbenzene solution: — — —, thermal, 70°; —, photochemical, 70°.

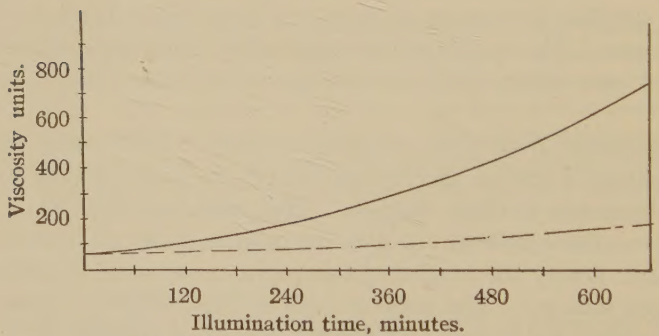

Fig. 2.—Polymerization of styrene–ethylbenzene solution: — — —, thermal, 70°; —, photochemical, 70°.

the results of two typical experiments. The straight lines were obtained from freezing point depression measurements while the curves record viscosity changes. The viscosity curve brings out the impossibility of using viscosity measurements to determine the rate of polymerization unless a viscosity–concentration curve has first been made.

There is a measurable thermal polymerization of styrene at 70 and 100° which must be taken into consideration when temperature coefficients are determined. At 30° no correction was necessary with styrene and at neither 40 nor 70° was a thermal correction necessary for vinyl acetate. From the freezing point depression curves, rates of reaction can be meas-

ured and from these temperature coefficients determined. The results are given in Table III. They have been corrected for thermal effect where necessary.

TABLE III

TEMPERATURE COEFFICIENT OF PHOTOCHEMICAL POLYMERIZATION

Solution	Temperature interval, °C.	Temp. coefficient per 10° rise
Styrene	30–100	1.30
Styrene	30–70	1.33
Styrene	70–100	1.27
Vinyl acetate	40–70	1.26

To interpret these results it is necessary to know whether the absorption of the solution changes with temperature, since the wave lengths involved are near the absorption limits of the solutions. To determine this, a monochromator was set up with a mercury arc as the source of light. The emitted light from the monochromator was focused upon a potassium hydride photo-electric cell. The recorder was a sensitive Moll galvanometer connected in series with the cell. No change in light absorption with temperature could be observed within the accuracy of the measurements, which was about 5%.

Effect of Concentration on Polymerization Velocity.—Solutions of several different concentrations were made and these were illuminated for the same length of time. The freezing point depression changes were determined and each polymerized solution was then diluted with ethylbenzene or ethyl acetate to a concentration of 10% by volume. The viscosities of these diluted solutions were thus determined at comparable concentrations. The results of these experiments are incorporated in Tables IV and V.

TABLE IV

CONCENTRATION–VELOCITY DATA FOR STYRENE IN ETHYLBENZENE

Concentration, %	Viscosity change, units	Change in dep. of f. p. of benzene, °C.
10	50	0.03
30	84	.16
65	150	.20
100	149	.305

TABLE V

CONCENTRATION–VELOCITY DATA FOR VINYL ACETATE IN ETHYL ACETATE

Concentration, %	Viscosity change, units	Change in dep of f. p. of benzene, °C.
13	20	0.10
65	44	.14
100	230	.45

To determine whether these results were due to concentration variations, to light absorption variations, or to both, monochromatic light was used

with an arrangement as described previously. A quartz vessel was used for the absorption cell and the loss due to reflection was obtained by measurement on the vessel filled with ethyl acetate and ethyl benzene, respectively. Measurements were made with solutions of three different concentrations and from these the absorption coefficients were calculated using the equation

$$I_{abs.} = I_{ent.}\ (1 - e^{-\alpha c})$$

where $I_{abs.}$ is the intensity of the absorbed light, $I_{ent.}$ is the intensity of the entering light, α is the absorption coefficient and c is the concentration of the absorbing constituent. The values of the coefficients are necessary to calculate the absorption for the lowest concentration of solution, since the absorption in this case was too low to measure accurately. In the following table these data are incorporated.

TABLE VI

ABSORPTION DATA FOR VINYL ACETATE IN ETHYL ACETATE

Concentration, %	3100 Å. Measured abs., %	3100 Å. Corrected abs., %	Coefficients	3600 Å. Meas. abs., %
0	10	..	....	..
13	..	6	0.00434	0
30	22.5	14	.0050	0
60	30.0	23	.00430	0
100	38.0	31	.00372	0
		Average	.00434	

TABLE VII

ABSORPTION DATA FOR STYRENE IN ETHYLBENZENE

Concentration, %	3100 Å. Measured abs., %	3100 Å. Corrected abs., %	Coefficient	3600 Å. Meas. abs., %
0	20	..	....	..
10	..	12	0.0125	2
30	44	30	.0119	9
60	66	57.5	.0140	17
100	75	69.0	.0115	20
		Average	.0125	

The above tables give all the data necessary to interpret the experiments which have been summarized in Tables IV and V.

Effect of Inhibitors.—Hydroquinone was selected as the inhibitor to be studied since it was found to have a large effect and, therefore, could be used in small concentrations. The experiments were made with 40% styrene solution at 100° and 30% vinyl acetate solution at 70°. Table VIII gives a summary of these results.

As shown by Anderson and Taylor,[7] an inhibitor may act in either or both of two ways. In one case it may cause a decrease in reaction rate by

[7] Anderson and Taylor, *J. Am. Chem. Soc.*, **45**, 650 (1923).

TABLE VIII

INHIBITORY EFFECT OF HYDROQUINONE

Styrene in ethylbenzene		Vinyl acetate in ethyl acetate	
Concentration of hydroquinone	% of normal polymerization rate	Concentration of hydroquinone	% of normal polymerization rate
1 mole in 160	2	1 mole in 150	2
1 mole in 400	24	1 mole in 300	10.8
1 mole in 800	49.1	1 mole in 1500	27.0
1 mole in 4000	86	1 mole in 3000	50.0

absorbing light which would otherwise be used to produce a reaction. In the other case it may cause a decrease in reaction rate by some inhibitor mechanism. Ratios of absorption of styrene or vinyl acetate to that of hydroquinone under the conditions of the experiments were not determined but the fact that hydroquinone does absorb[8] seems to explain the relationship between concentrations of inhibitor and reaction rate. This will be discussed later.

Quantum Yields in the Polymerization.—A series of experiments was made to find the variation of quantum yield with wave length of absorbed light. The first measurements were made with the line of wave length 2300 Å. The source of the energy was a high voltage interrupted spark discharge across cadmium electrodes in air, constructed by Dr. G. B. Kistiakowsky. In order to determine the quanta which fell upon the system, it was desired to use the decomposition of oxalic acid sensitized with uranyl ions. This has been shown by Bowen and Watts[9] to have a quantum yield of one and a temperature coefficient of unity in the near ultraviolet.[10] Experiments made in light of wave length 2300 to 2500 Å. indicated that for our purpose the value of Bowen and Watts could be employed.

Quantum yield measurements were made at $\lambda = 2536$ Å. with both vinyl acetate and styrene. For this a hot mercury arc and chlorine–bromine filter were used. A correction was made for the visible light which passed through the filter and the decomposition of oxalic acid–uranyl acetate solutions was used to determine the number of quanta falling on the system. The absorption of the 2536 Å. line was measured by means of a thermopile.

Finally the quantum yield was determined when exposed to the mercury arc as in the original experiments. This is designated as the quantum yield at wave lengths between $\lambda = 3000$ Å. and $\lambda = 4000$ Å. Pure styrene and pure vinyl acetate were exposed in a quartz reaction cell. This cell was immersed in a Pyrex water-bath and thus the conditions of the original

[8] "International Critical Tables," Vol. V, p. 361.

[9] Bowen and Watts, *J. Chem. Soc.*, **129**, 1607 (1926).

[10] Recently Leighton and Forbes [*J. Am. Chem. Soc.*, **52**, 3139 (1930)] have found that a more careful determination indicates a quantum yield of 0.49 to 0.60 in ultraviolet light. However, since the polymerization quantum yields here presented are only orders of magnitude, the value of Bowen and Watts is sufficiently accurate.

experiments were reproduced. The results of these experiments are summarized in Table IX.

TABLE IX

POLYMERIZATION QUANTUM YIELDS

Wave length, A.	Vinyl acetate Yield, molecules/$h\nu$	Temp., °C.	Remarks	Styrene Yield, molecules/$h\nu$	Temp., °C.	Remarks
2300	1.7	50	Pure liquid	...	..	.....
2536	1.2	50	Pure liquid	7.4	70	40% solution
3000–4000, inc.	935	65	Pure liquid	4.0	90	Pure liquid

Discussion

Effect of Oxygen.—Moureu and Dufraisse[4] pointed out the effect of oxygen upon the photo-polymerization of acrolein and found that small amounts of this gas caused a very great increase in rate of polymerization. Since then there has been a tendency to attribute photo-polymerization to peroxide formation. No objection, theoretically, can be advanced against assuming that polymerization can occur as a consequence of molecules initially activated by light. The experiments described in this paper represent the distinct separation of these two methods of polymerization. It seems well established that polymerization may be induced by light which is absorbed by the molecules in question and that all the data of this paper represent the various phases of such a process.

Effect of Temperature.—The curves of Fig. 1 and Fig. 2 are typical of those from which the values of Table II were calculated. Calculations were made from the viscosity curves to find how the viscosity of the solution changed with temperature for the same percentage polymerization as shown by freezing point depression measurements. The results of the calculations are given in Tables X and XI. The values for the percentages

TABLE X

CHANGE IN SIZE OF POLYMER WITH TEMPERATURE FOR STYRENE SOLUTION

Total % polymer	Viscosity change at 30°, units	70°, units	100°, units
1.35	5	8	20
3.37	15	26	60
6.75	40	72	135
10.6	80	130	200
16.9	245	290	480
21.2	320	450	760

TABLE XI

CHANGE IN SIZE OF POLYMER WITH TEMPERATURE FOR VINYL ACETATE SOLUTION

Total % polymerized	Viscosity change at 40°, units	70°, units
14.3	220	220
42.9	2000	1440
57.2	4000	2800

where the viscosity change is less than 50 units are subject to a large error of reading. The other values represent reliable data.

An examination of these tables would seem to indicate that the aggregates of styrene are of a much larger size at high than at low temperatures. This would be different from the thermal polymerization as studied by Staudinger.[6] However, any more definite conclusions from these tables must wait for more experiments to determine completely this viscosity relationship. It would seem that, for styrene, the photochemical effect is stronger than the thermal, while for vinyl acetate the thermal effect somewhat overbalances the photochemical. It is evident, in any case, that the temperature effect is much different in the case of styrene than in the case of vinyl acetate.

Effect of Concentration on Reaction Velocity.—The change in reaction rate with concentration is due entirely to the change in absorption of light with concentration. This is evident by comparing Tables VI and VII with Tables IV and V.

A calculation of per cent. polymerized at the various concentrations shows a practically constant value. This lends further proof to the explanation given previously.

Effect of Inhibitor.—Inhibition which was due to deactivation by collision with the foreign molecules would be inversely proportional to the inhibitor concentration. If the inhibitor also acted in some other way as, for example, by screening, the decrease in reaction rate would be correspondingly greater. Table VIII shows that for styrene solutions a change of inhibitor concentration from 1 molecule in 160 to 1 molecule in 400 produced over a ten-fold change in reaction velocity. A similar effect is evident for vinyl acetate.

Since the only factors present in our case were deactivation by collision and screening by absorption of the active light, it seems clear that the inhibiting effect was due to both of these causes. The belief that hydroquinone could deactivate by collision was further substantiated by the results of some thermal experiments. In these tests it was found that hydroquinone was effective in preventing the thermal polymerization when present in concentrations of the order of magnitude of 1 molecule in 1000.

Quantum Yields.—The quantum yields given in Table IX represent the number of molecules which gather together as a result of the absorption of one quantum of light energy. The values of Table IX are in all cases upper limits of the quantum yields. The low quantum yield of vinyl acetate in light of wave lengths shorter than 3000 Å. was probably due to decomposition.

An example of the quantum yield calculations is given below.

Quantum Yield of Vinyl Acetate Polymerization at λ = *3000–4000 Å.*—1. Quanta absorbed by vinyl acetate in one hour as determined from oxalic acid–uranyl acetate

experiment and measurements of the relative absorption of vinyl acetate and oxalic acid solution were 1.07×10^{19}.

2. (a) Initial depression of freezing point of benzene due to 1 cc. of vinyl acetate in 25 cc. of benzene = 2.095°.

(b) Change in depression after illumination for one-half hour = 0.11°.

(c) Temperature = 65°.

(d) Grams of vinyl acetate exposed = 13.5 g.

Therefore the number of molecules of vinyl acetate polymerized in one hour

$$2 \times \frac{0.11}{2.095} \times \frac{13.5}{86.06} \times 6.06 \times 10^{23} = 1.0 \times 10^{22}$$

$$\text{Hence, the quantum yield at } 65° = \frac{1.00 \times 10^{22}}{1.07 \times 10^{19}} = 935 \frac{\text{molecules}}{h\nu}$$

Conclusions

The photochemical polymerization results which have been presented indicate that the polymerization process has many of the characteristics of a chain mechanism. The initially activated molecule initiates the reaction by combining with another molecule. This process is exothermic and as a result these two are energy-rich and can add a third to their aggregate. This addition process continues until the energy of the group is insufficient to cause the addition of another member. This loss of energy may be caused by collision with foreign molecules of the solvent, by collision with the walls or by distribution over the whole aggregate to such an extent that further reaction is impossible.

The author wishes to express his thanks to Dr. G. B. Kistiakowsky for his aid in developing the experimental procedure and interpreting the results.

Summary

1. Several phases of the photochemical polymerization of styrene and vinyl acetate have been investigated. A method of studying photochemical polymerizations has been developed which gives reproducible results and avoids all effects due to oxygen absorption.

2. Oxygen aids but is not necessary for the photo-polymerization of styrene.

3. Oxygen inhibits the photo-polymerization of vinyl acetate.

4. Both reactions have temperature coefficients markedly greater than unity.

5. The effect on the reaction velocity of a change in concentration of polymerizing constituent depends upon the change of light absorption with concentration of that constituent.

6. The orders of magnitude of the quantum yields have also been determined for several wave lengths. They indicate clearly that the polymerization process involves a chain mechanism.